Computer studies of fluctuation of confined fluid

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熱場の量子論 2019/9/4

in collaboration with Shin-ichi Sasa

Boundary condition on Navier-Stokes equation

Macroscopic behavior of fluids is described by NS equation.

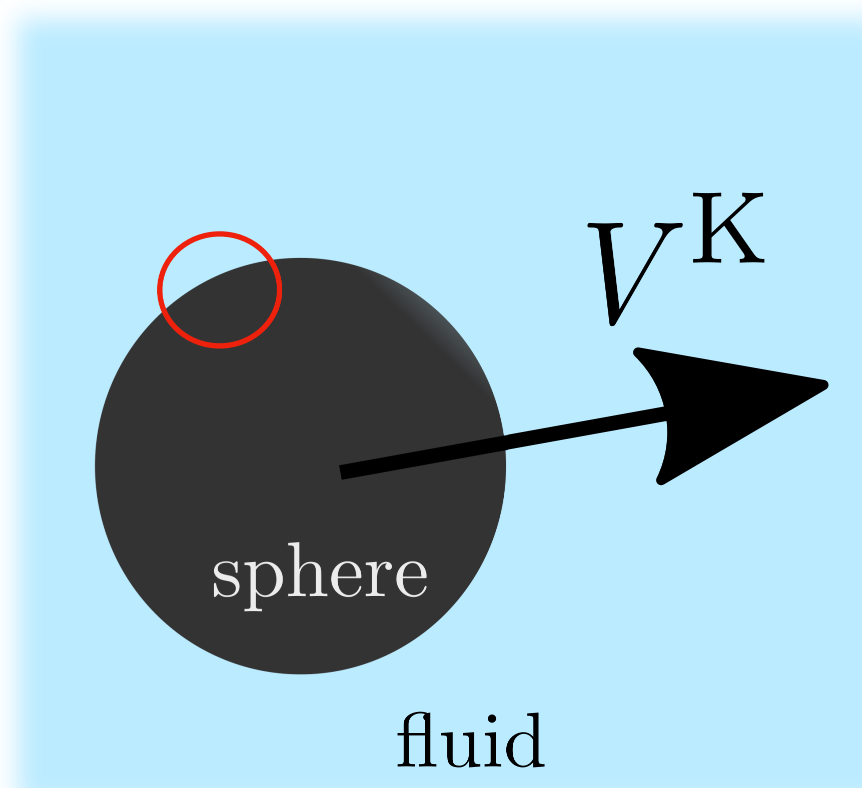
incompressible fluid $\longrightarrow$ $\rho = \mathrm{const}$

$$\boldsymbol{\nabla} \cdot \boldsymbol{v} = 0$$

$$\frac{\partial \boldsymbol{v}}{\partial t} + (\boldsymbol{v} \cdot \boldsymbol{\nabla})\boldsymbol{v} = -\frac{1}{\rho}\boldsymbol{\nabla} p + \frac{\eta}{\rho}\Delta \boldsymbol{v}$$

Boundary condition

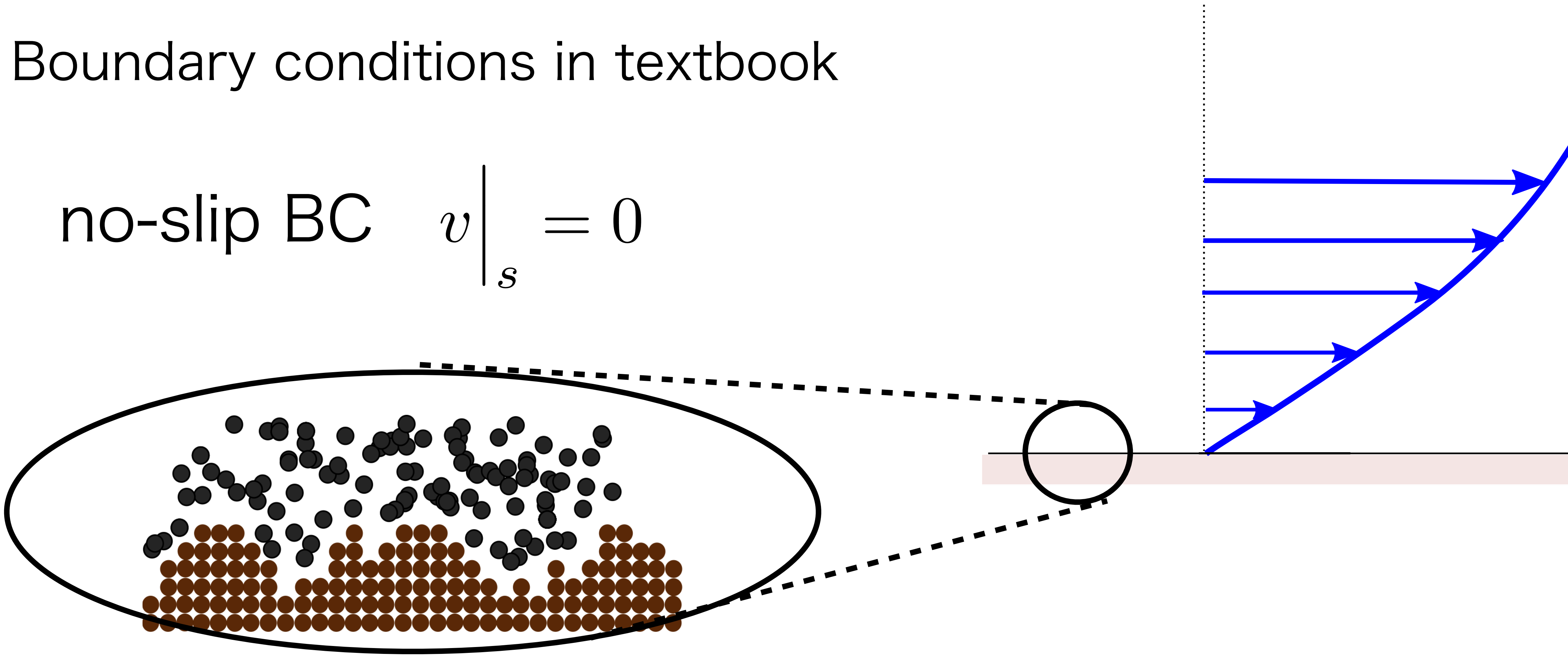
Motion of fluid at solid surface



Motivation for investigation of boundary condition

Boundary conditions in textbook

no-slip BC $\quad v\Big|_s = 0$



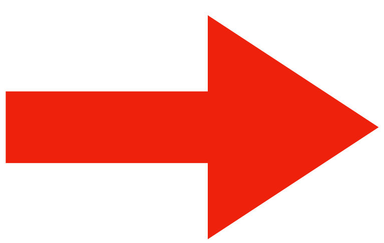
Surface roughness brings fluid to rest.

Development of nanotechnology from 1990s

・control of roughness

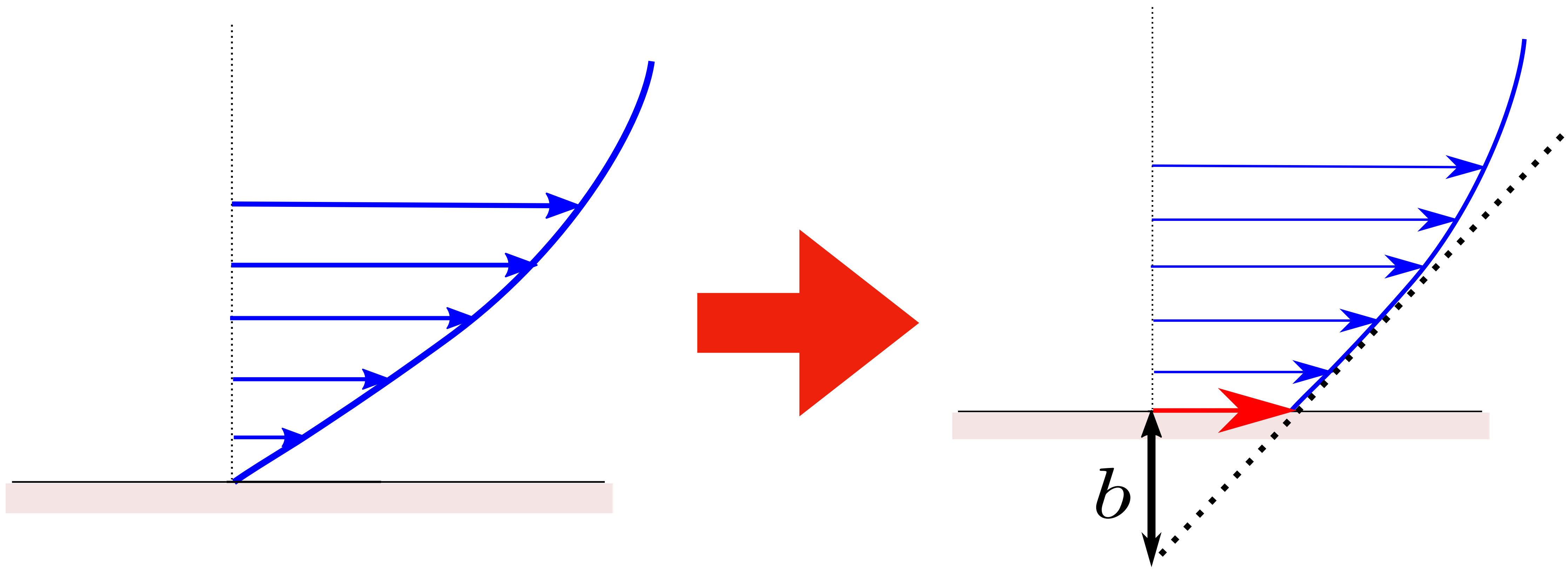
・increasing of measurement accuracy

(Zhu and Granick, 2001)



breakdown of no-slip BC

New transport coefficient



no-slip BC

$$v\Big|_s = 0$$

partial slip BC

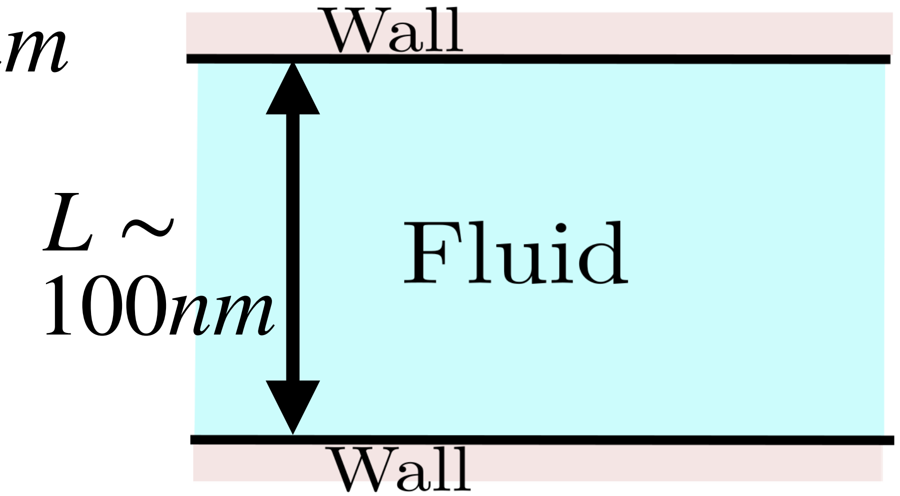
$$v\Big|_s = b\frac{dv}{dz}\Big|_s$$

・Slip length is new transport coefficient that characterizes the amount of slip. (cf. viscosity, thermal conductivity)

・No-slip BC is a special case of partial slip BC. ($b = 0$)

Application of slip phenomena

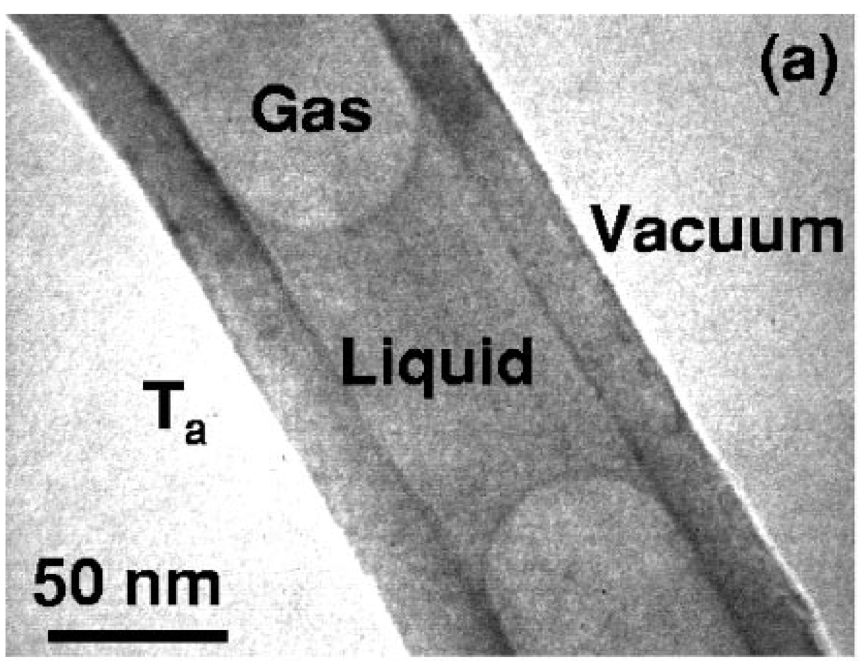
Typically, slip length is about $0nm \sim 30nm$



Nano- and Microfluidics

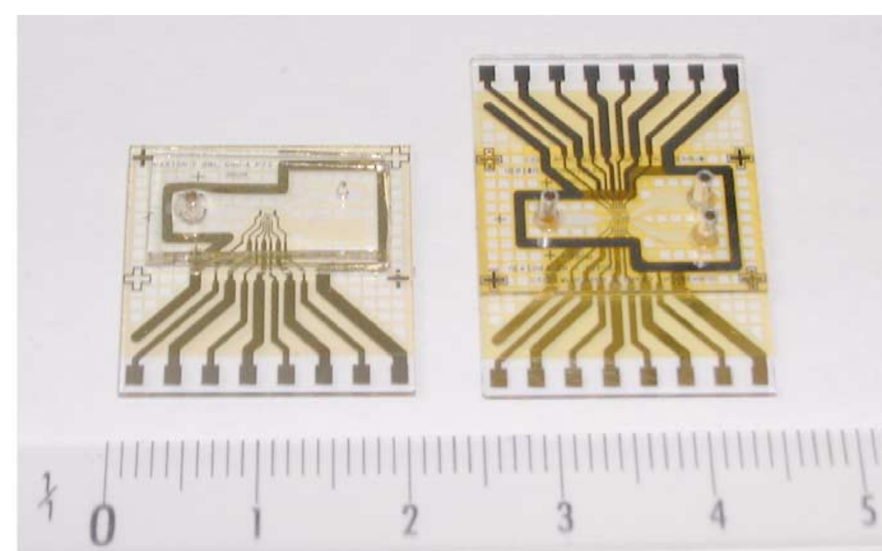
Control and manipulation of fluids at submicron scale

$\longrightarrow$ Slip length becomes a new variable to be user-controlled.



Y. Gogotsi et al., Appl. Rhys. Lett. **79**, 1021 (2001)

Lab-on-a-chip devices



(a)

S. Gawad et al., Lab. Chip **1**, 76(2001)

Theme of this presentation

Our goal : to establish relationship between slip length and
molecular parameters(wall structure, fluid structure)

<u>Tools</u>

Molecular dynamical simulation

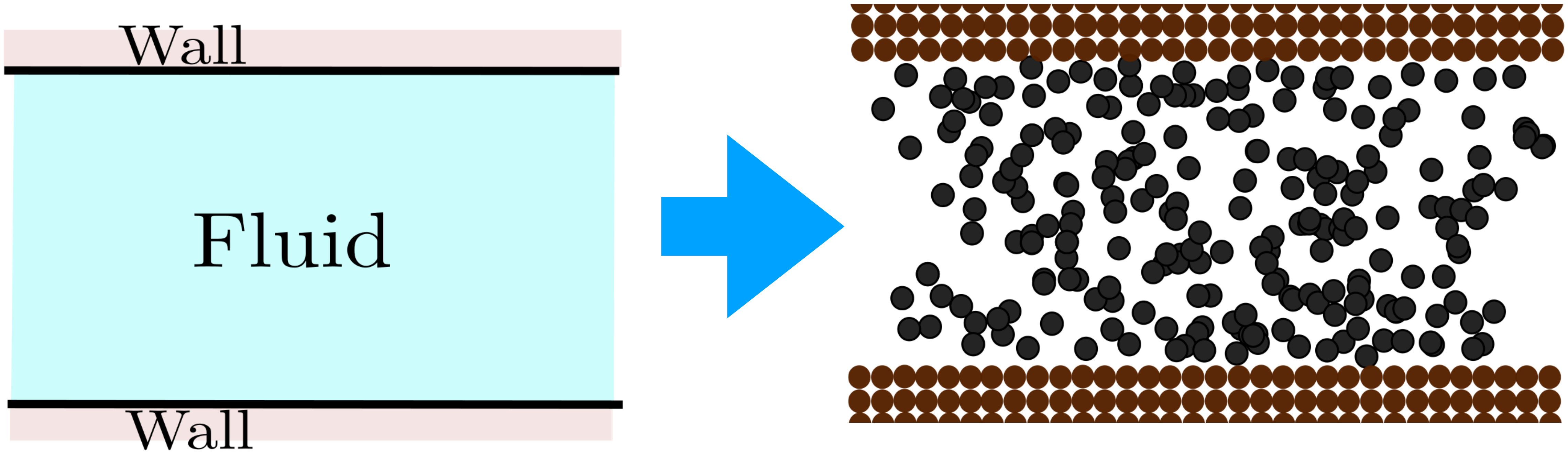
Green-Kubo formula

Linearized fluctuating hydrodynamics

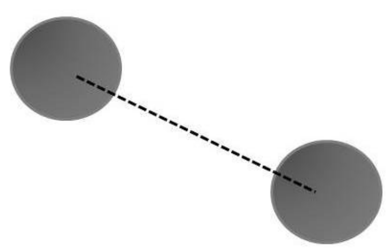
Previous studies

Our proposal

Molecular dynamical simulation

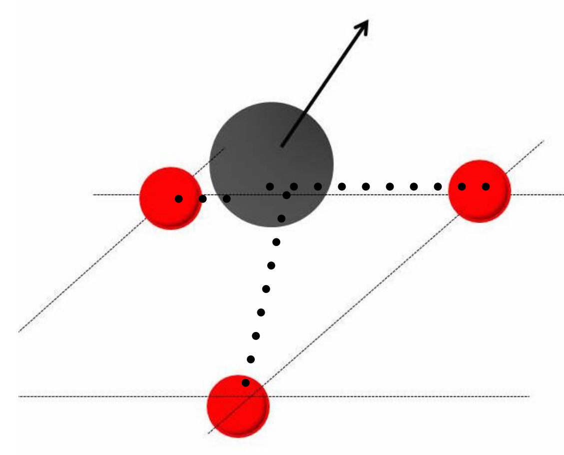


square lattice



Interaction between fluid particles

$$V(r) = 4\epsilon\left\{\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right\}$$

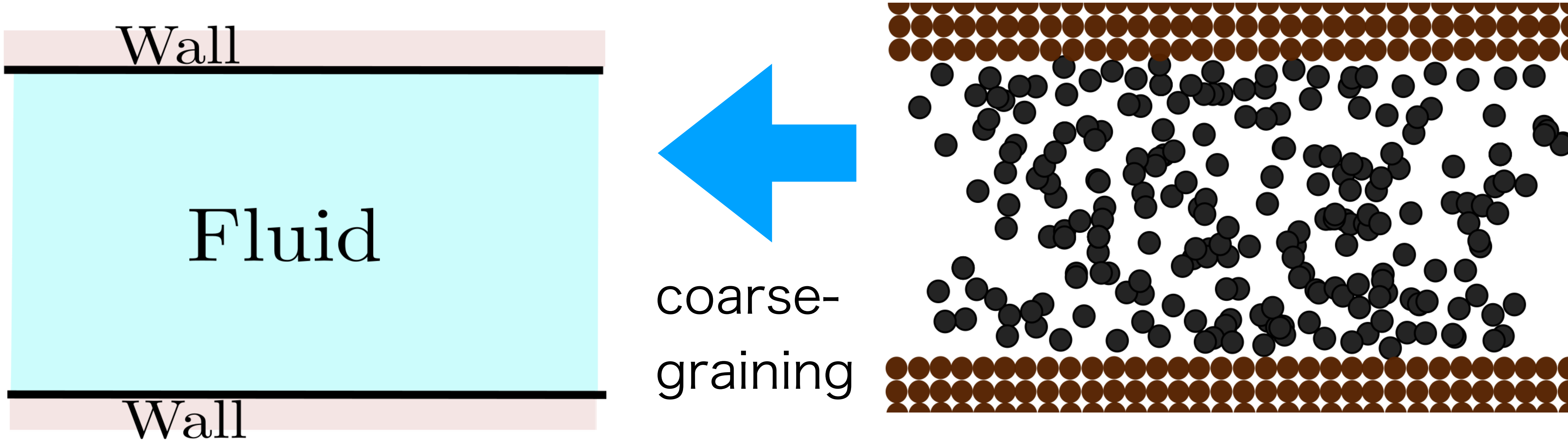


interaction between fluid particle and solid particles

$$V_{\mathrm{FS}}(r) = 4\epsilon\left\{\left(\frac{\sigma_{\mathrm{FS}}}{r}\right)^{12} - c_{\mathrm{FS}}\left(\frac{\sigma_{\mathrm{FS}}}{r}\right)^{6}\right\}$$

Microscopic description: Hamilton's equation

Green-Kubo formula



Kirkwood (1946), Zwanzig (1960)

<u>GK formula for slip length</u>

$$\frac{\eta}{b} = \frac{1}{k_B T S} \lim_{t\to\infty} \lim_{L\to\infty} \int_0^t ds \langle \hat{F}_t(s) \hat{F}_t(0) \rangle$$

System size is **macroscopic**.

$\hat{\boldsymbol{F}}(t)$

microscopic force acting on wall

Bocquet and Barrat (1994)

Nakano and Sasa (2019)

GK formula × MD simulation

is very difficult, mainly because of macroscopic limit.

GK formula for slip length

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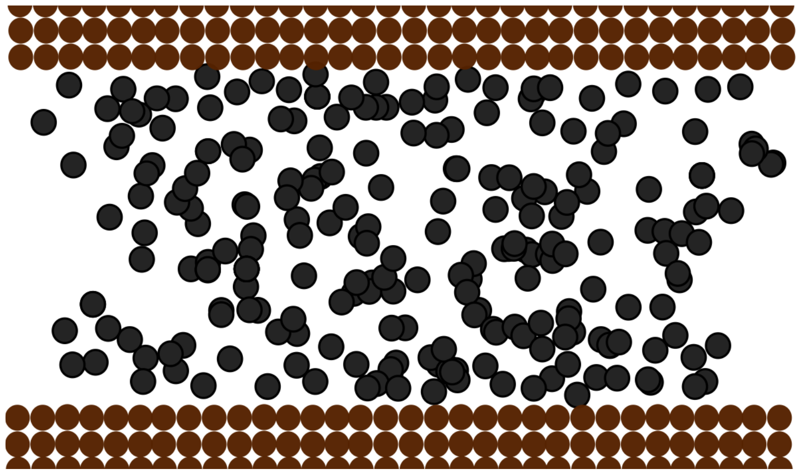


Calculation method

1, prepare equilibrium state at $t = 0$

2, calculate microscopic force $\hat{\boldsymbol{F}}(t)$ from snapshot

3, calculate force autocorrelation function

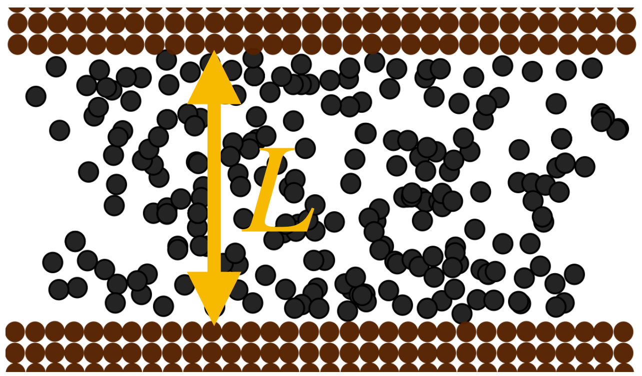
$$\langle \hat{\boldsymbol{F}}(t) \hat{\boldsymbol{F}}(0) \rangle_{\mathrm{eq}} = \frac{1}{\Delta T} \int_0^{\Delta T} ds \hat{\boldsymbol{F}}(t+s) \hat{\boldsymbol{F}}(s)$$

4, calculate time integral

$$\gamma(t) = \frac{1}{k_B T S} \int_0^t ds \langle \hat{F}_t(s) \hat{F}_t(0) \rangle$$

Calculation result

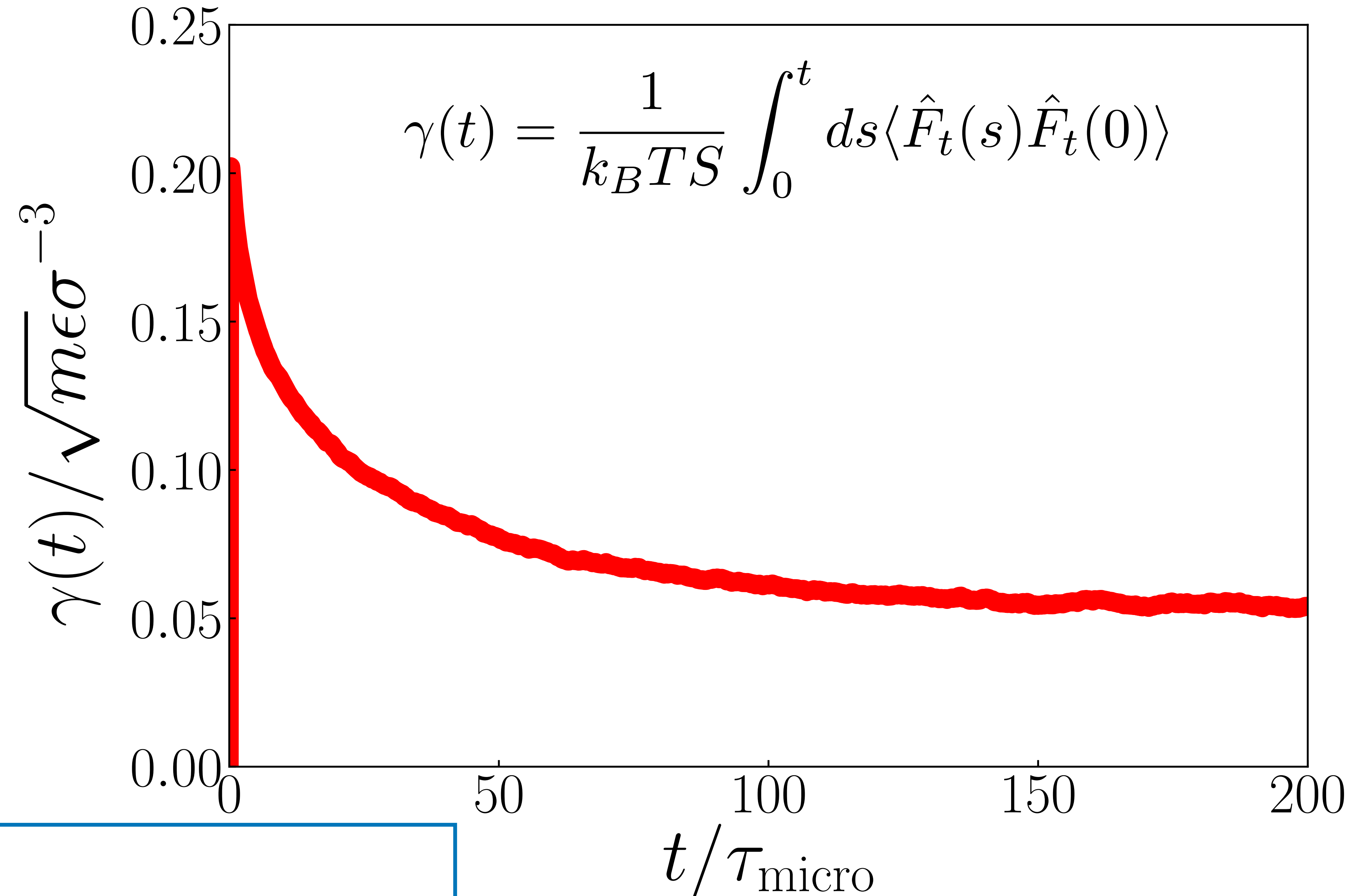
Parameters



$$L = 20.0\sigma$$

$$(L_x, L_y) = (48.0\sigma, 48.0\sigma)$$

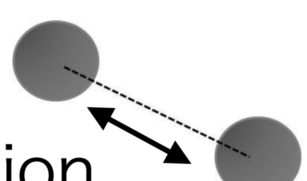
$$\rho = 0.75\sigma^{-3}$$



Units

length: diameter of fluid particle σ

time: microscopic time τ_{micro}



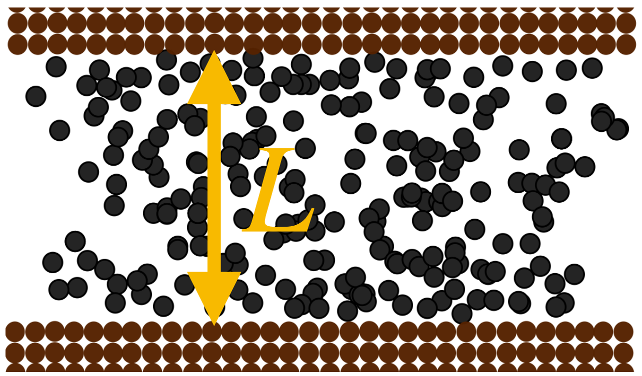
$0.83\tau_{\mathrm{micro}}$

GK formula for slip length

$$\frac{\eta}{b} = \lim_{t\to\infty}\lim_{L\to\infty}\gamma(t)$$

Calculation result

Parameters



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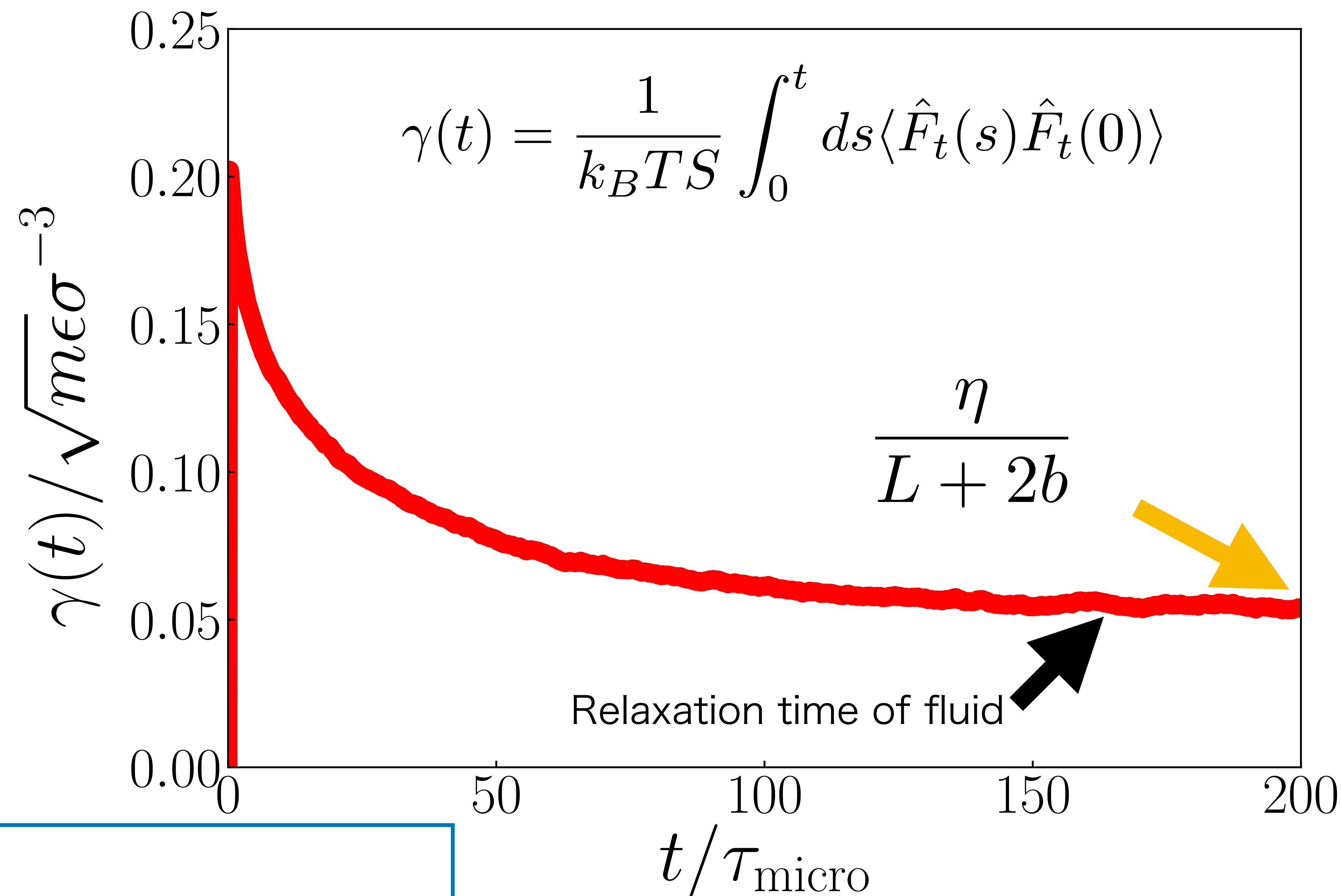

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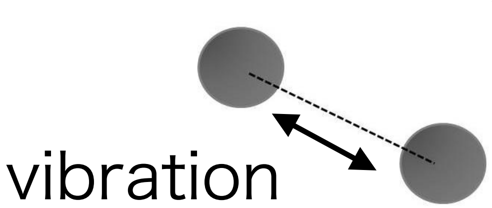

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<u>GK formula for slip length</u>

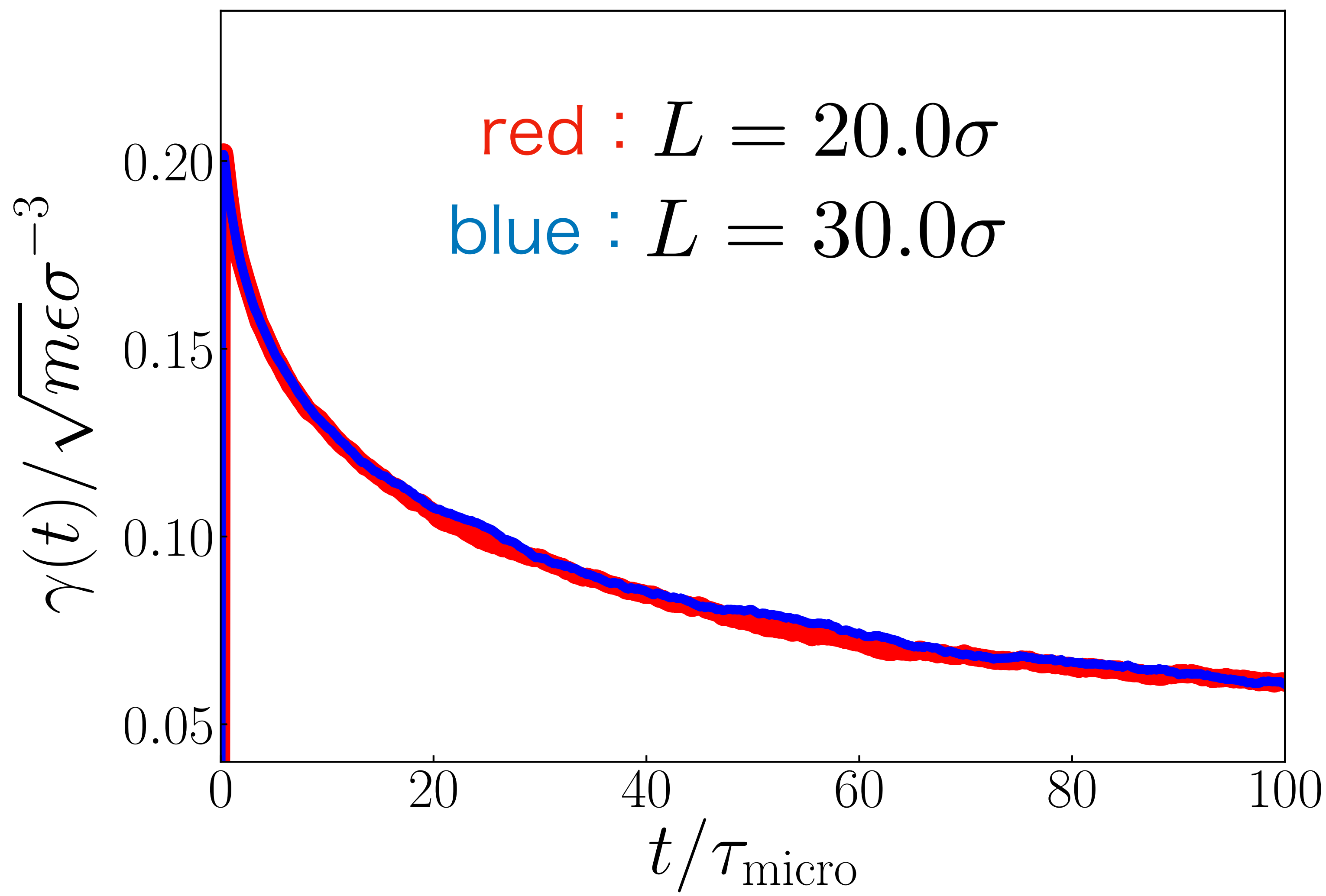
$$\frac{\eta}{b} = \lim_{t\to\infty} \cancel{\lim_{L\to\infty}} \gamma(t)$$

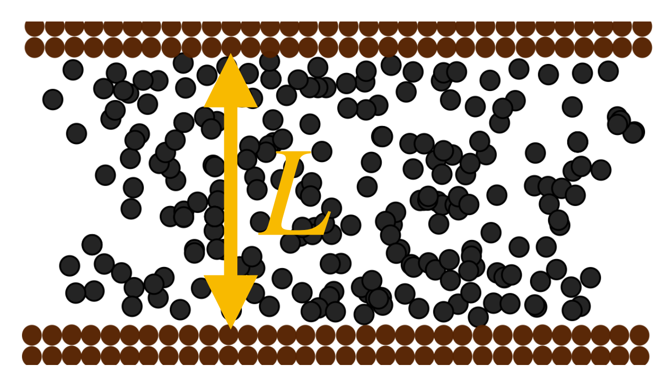
System Size Dependence

GK formula for slip length

$$\frac{\eta}{b} = \lim_{t\to\infty} \lim_{L\to\infty} \gamma(t)$$

High computational cost





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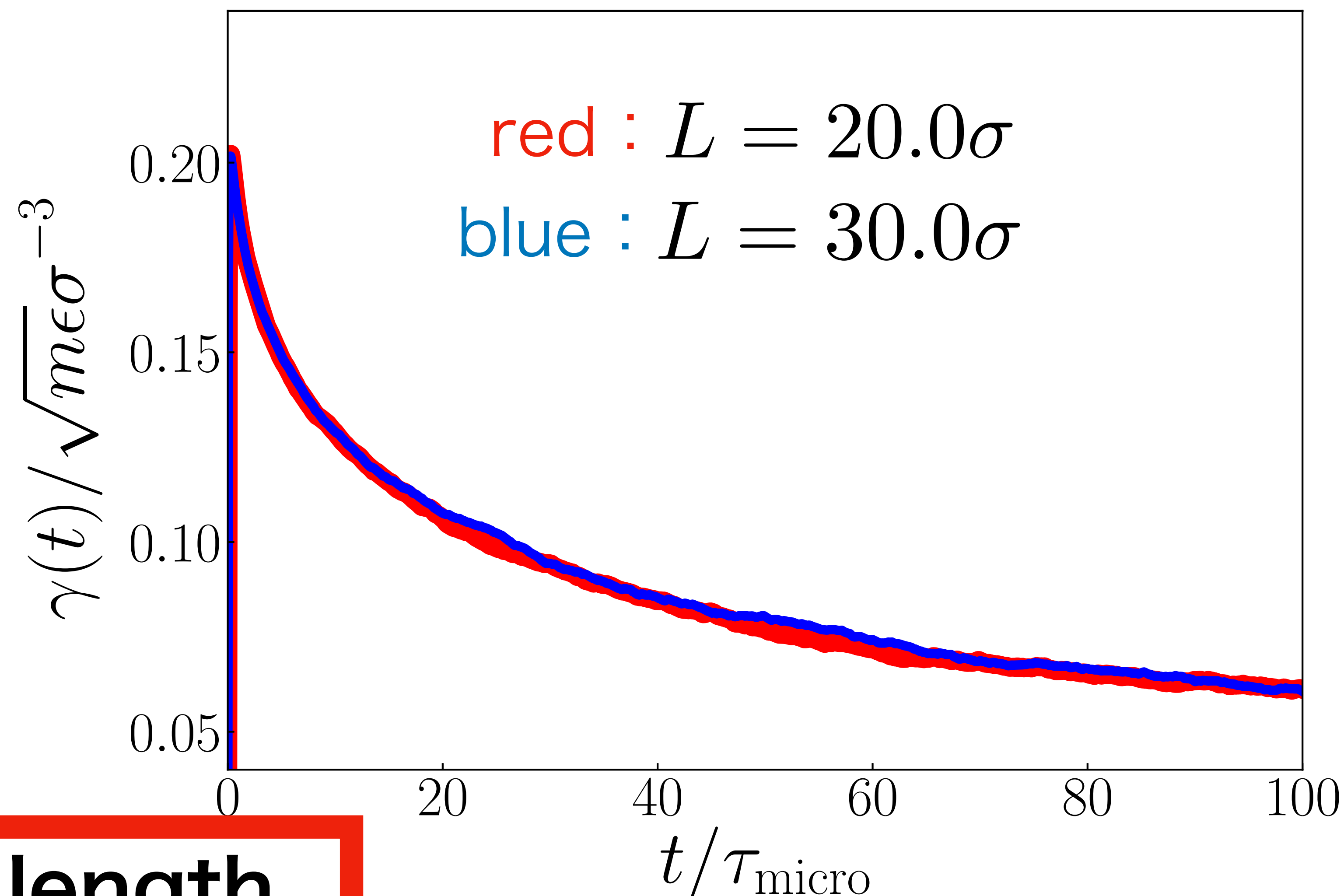
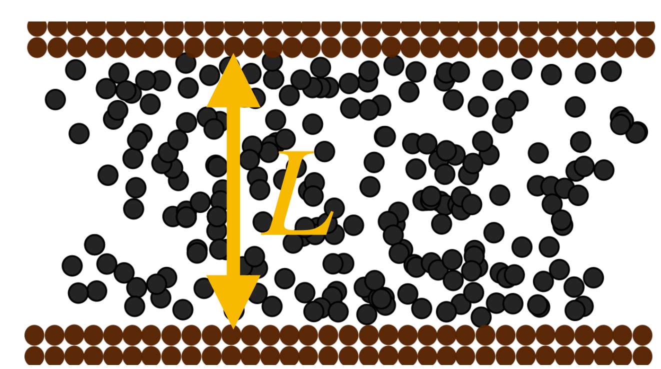


Where is correct slip length obtained?



GK formula is not practical.

New strategy

Our goal：to establish relationship between slip length and molecular parameters(wall structure, fluid structure)

↓

to extract information on slip length from $\gamma(t)$

<u>Tools</u>

Previous studies

Molecular dynamical simulation

Linearized fluctuating hydrodynamics

~~Green-Kubo formula~~

Our proposal

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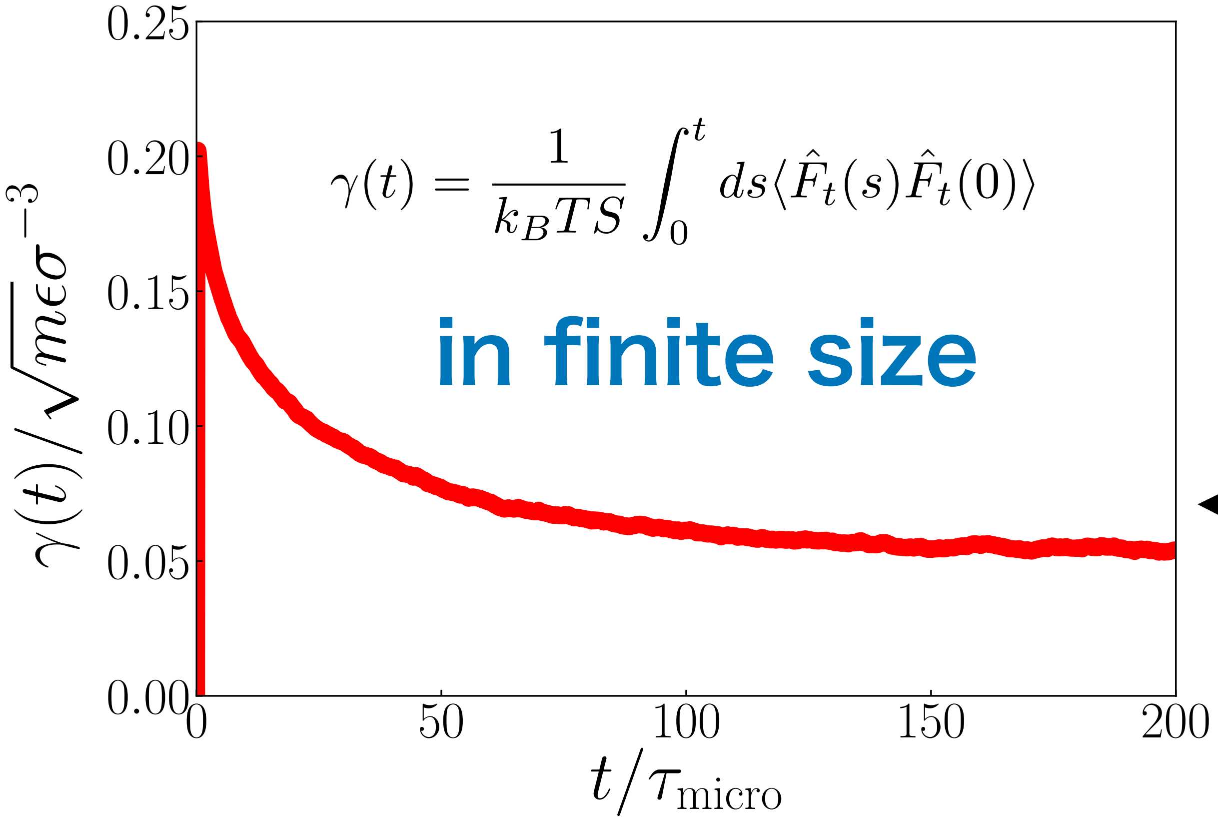
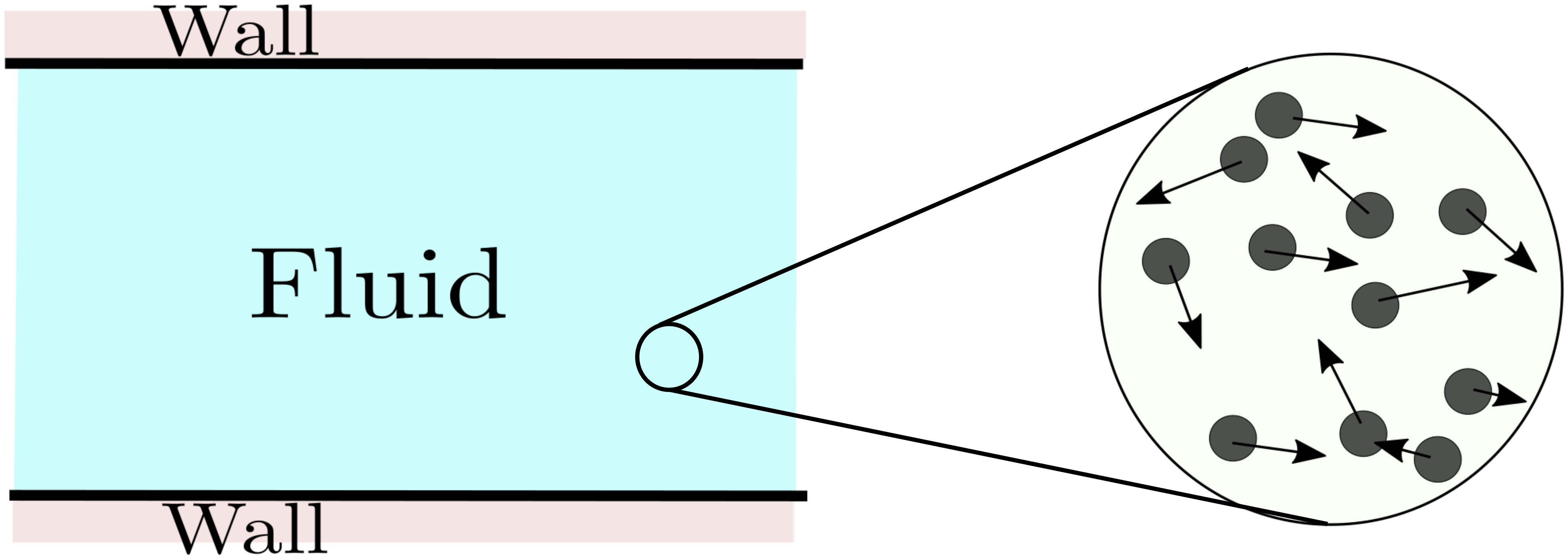


Linearized fluctuating hydrodynamics ← **describes this data**

Fluctuating hydrodynamics

Continuum description of fluctuation

Landau and Lifshitz, 1959



Navier-Stokes equation + fluctuation

$$\nabla \cdot \boldsymbol{v} = 0$$

$$\frac{\partial \boldsymbol{v}}{\partial t} + (\boldsymbol{v} \cdot \nabla)\boldsymbol{v} = -\frac{1}{\rho}\nabla p + \frac{\eta}{\rho}\Delta \boldsymbol{v} + \boldsymbol{f}$$

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Fluctuating hydrodynamics

Properties of fluctuation

0, Gaussian white noise 1, detailed balance condition

2, conserve law of momentum 3, isotropic properties of bulk

$$f^a(\boldsymbol{r},t)=\frac{\partial s^{ab}(\boldsymbol{r},t)}{\partial r^b}$$

$$\langle s^{ab}(\boldsymbol{r}_1,t_1)s^{cd}(\boldsymbol{r}_2,t_2)\rangle=2k_BT\eta\Big(\delta_{ac}\delta_{bd}+\delta_{ad}\delta_{bc}+\frac{2}{3}\delta_{ab}\delta_{cd}\Big)\delta(\boldsymbol{r}_1-\boldsymbol{r}_2)\delta(t_1-t_2)$$

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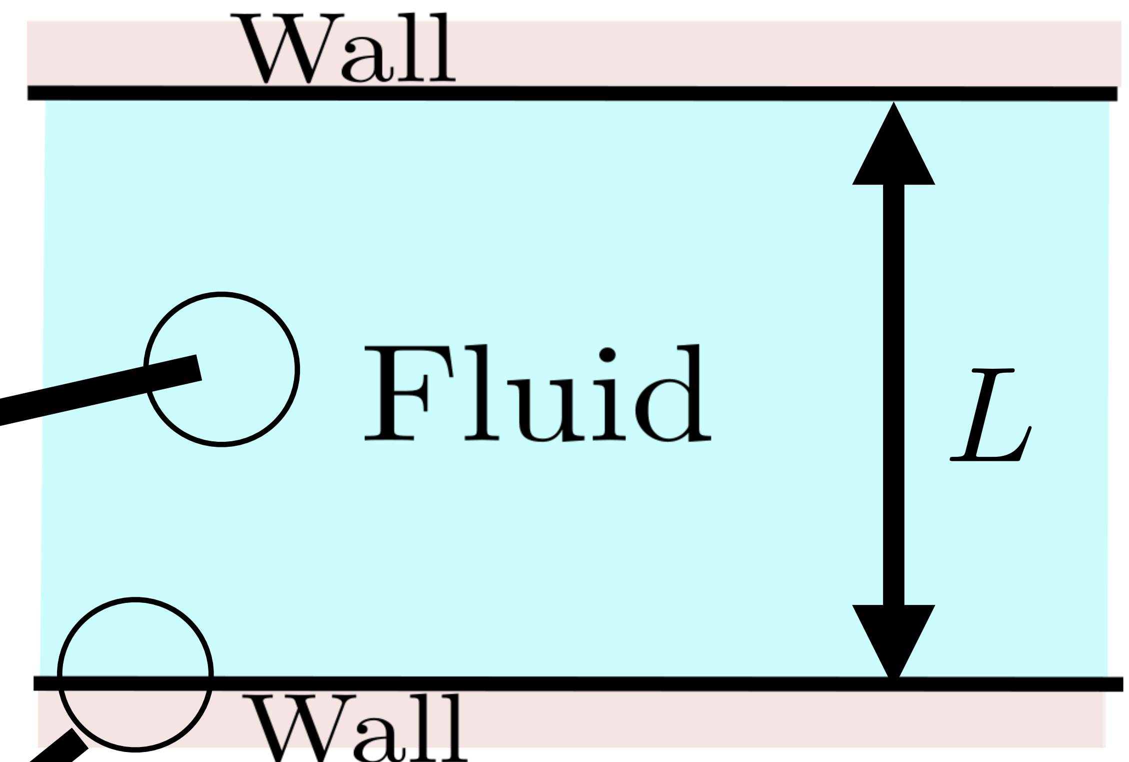
Fluctuation of confined fluids

Nakano and Sasa (2019)

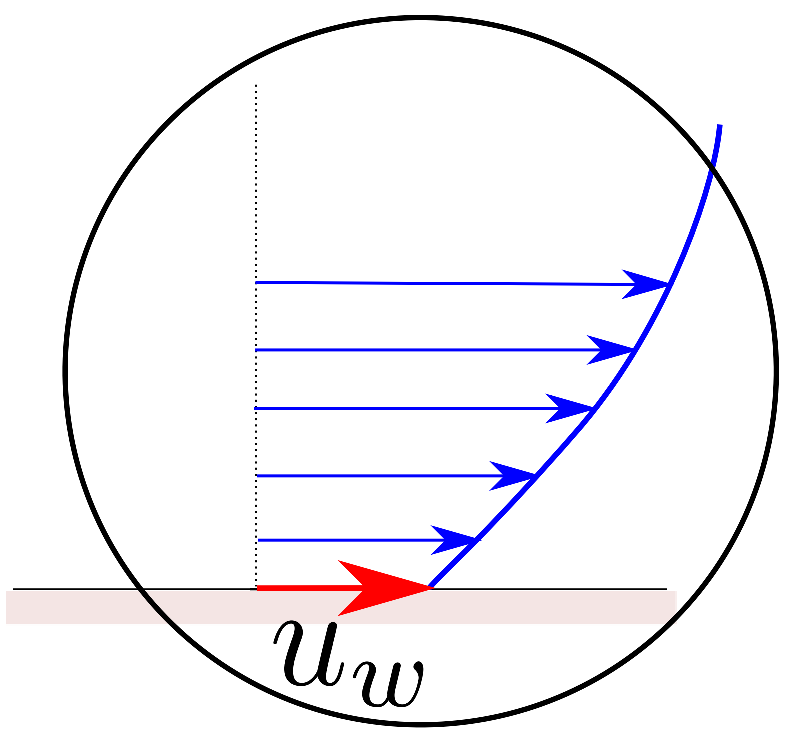


Linearized fluctuating hydrodynamics

$$\nabla \cdot \boldsymbol{v} = 0$$

$$\frac{\partial \boldsymbol{v}}{\partial t} = -\frac{1}{\rho}\nabla p + \frac{\eta}{\rho}\Delta \boldsymbol{v} + \boldsymbol{f}$$

Deterministic partial slip BC



$$v\Big|_s = b\frac{dv}{dz}\Big|_s$$

Force acting on wall

$$F_t = \int_S dxdy\left(\eta\frac{\partial v^x}{\partial z} + s^{xz}\right)\Big|_{\mathrm{wall}}$$

Exact calculation

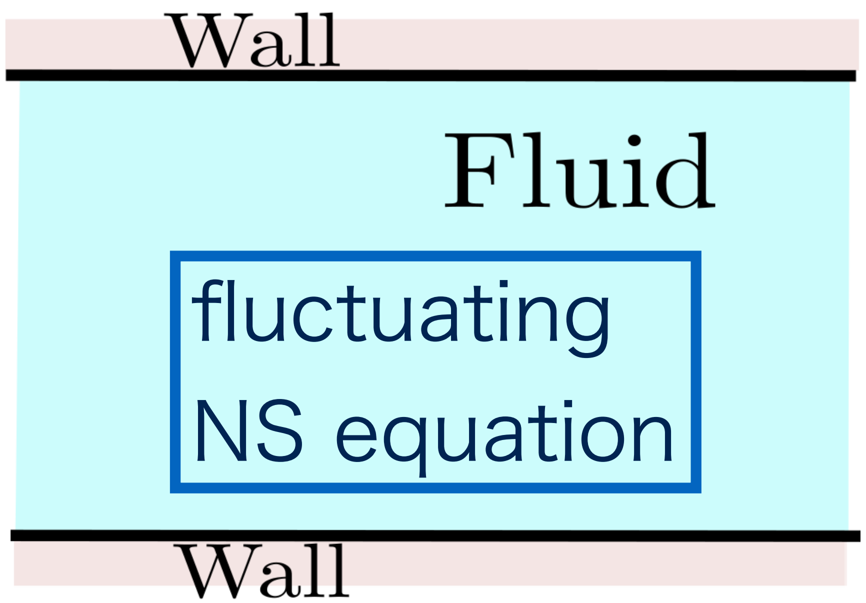
$$\gamma(t) = \frac{1}{k_B T S}\int_0^t ds\langle \hat{F}_t(s)\hat{F}_t(0)\rangle$$

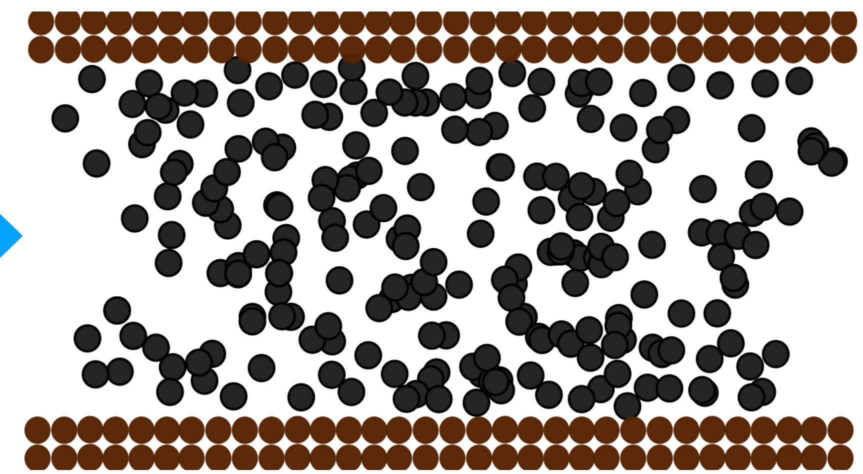
Fluctuating hydrodynamics

×

MD simulation

Comparison between simulation data and fluctuating hydrodynamics





Exact solution

$$\gamma(t) = \frac{1}{k_B T S} \int_0^t ds \langle \hat{F}_t(s) \hat{F}_t(0) \rangle$$

simulation

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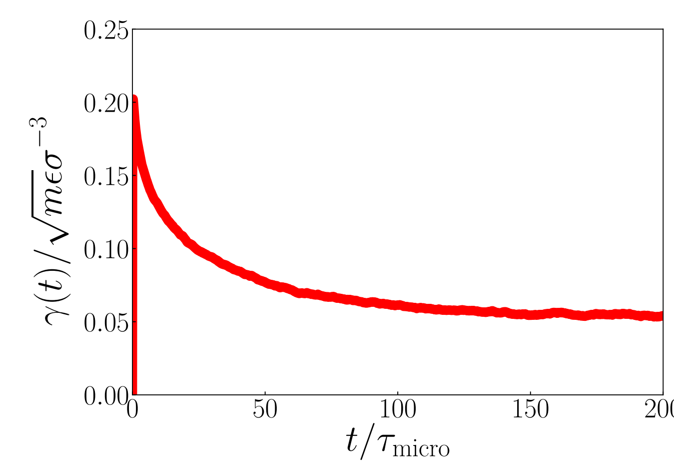
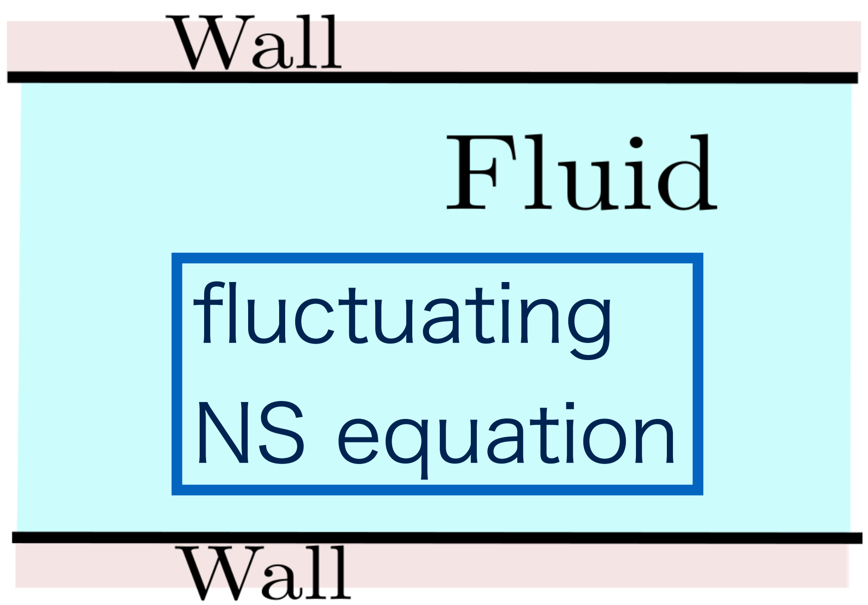
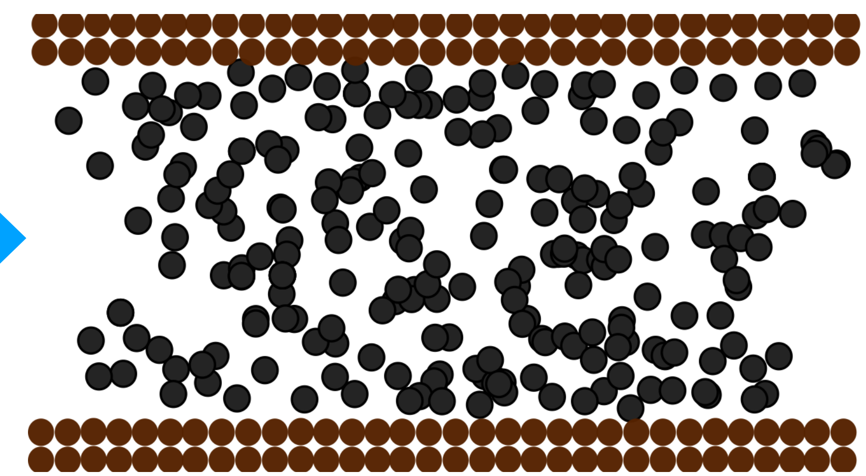


Comparison between simulation data and fluctuating hydrodynamics





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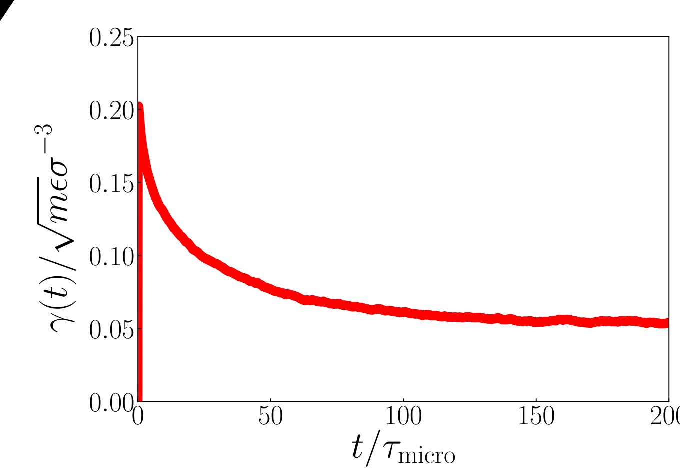
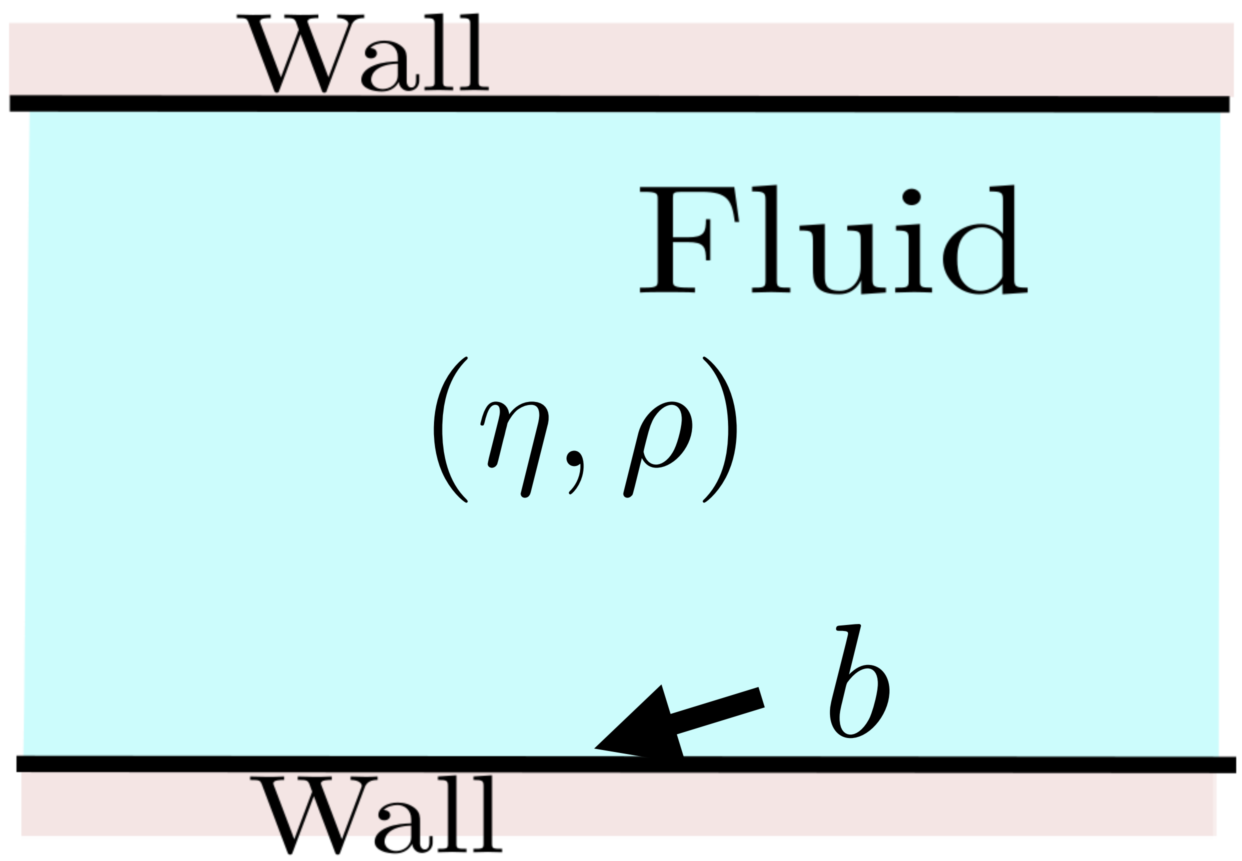
Fitting



Fitting parameter



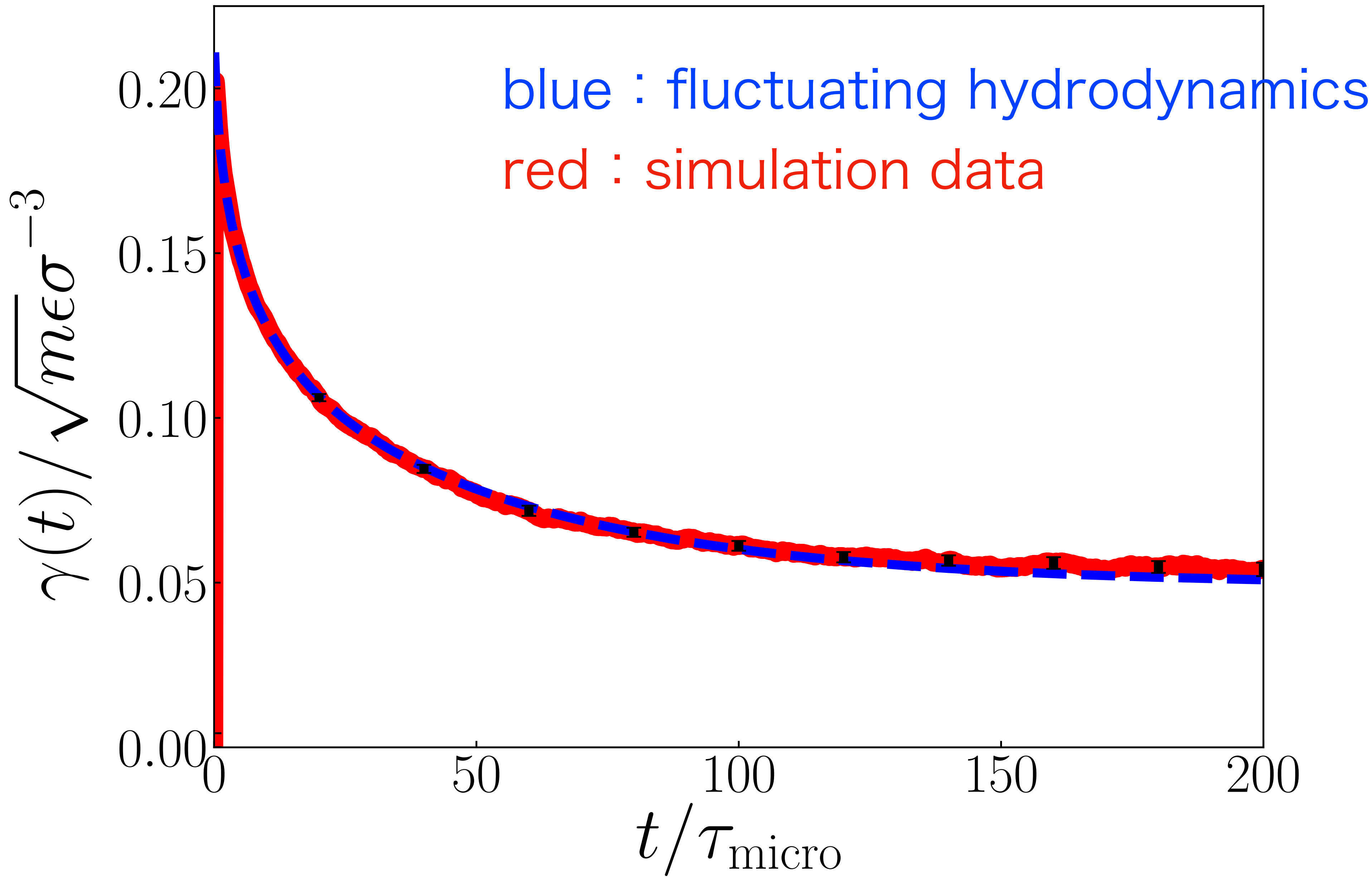
Parameters

η : viscosity in bulk, obtained in advance

ρ : density in bulk, obtained from simulation data

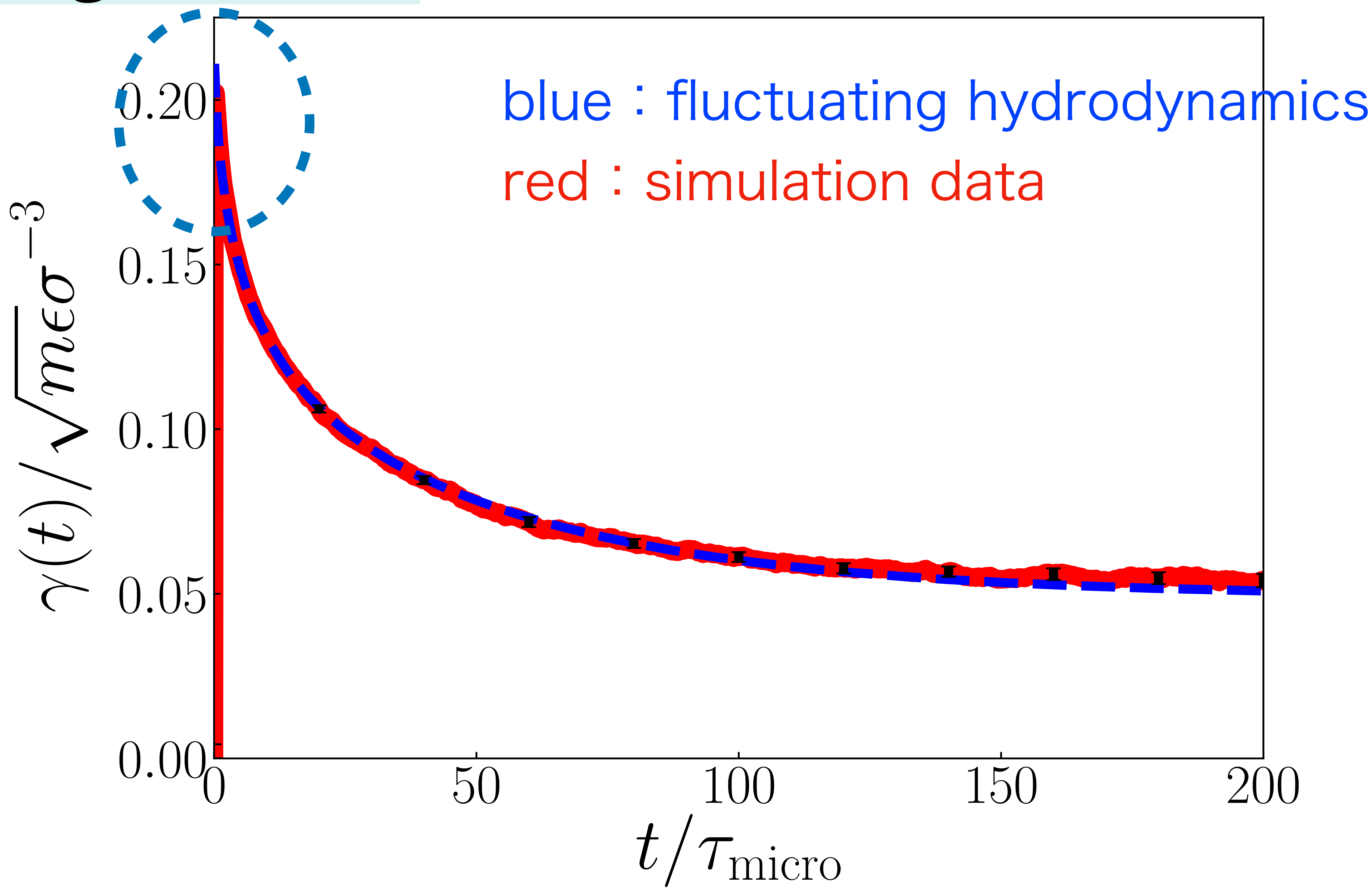
b : slip length $\longrightarrow$ fitting parameter

Fitting Results



Fluctuating hydrodynamics reproduces simulation data in full time region.
Fluctuation of force acting on wall is characterized by only three parameters (η, ρ, b).

Fitting Results



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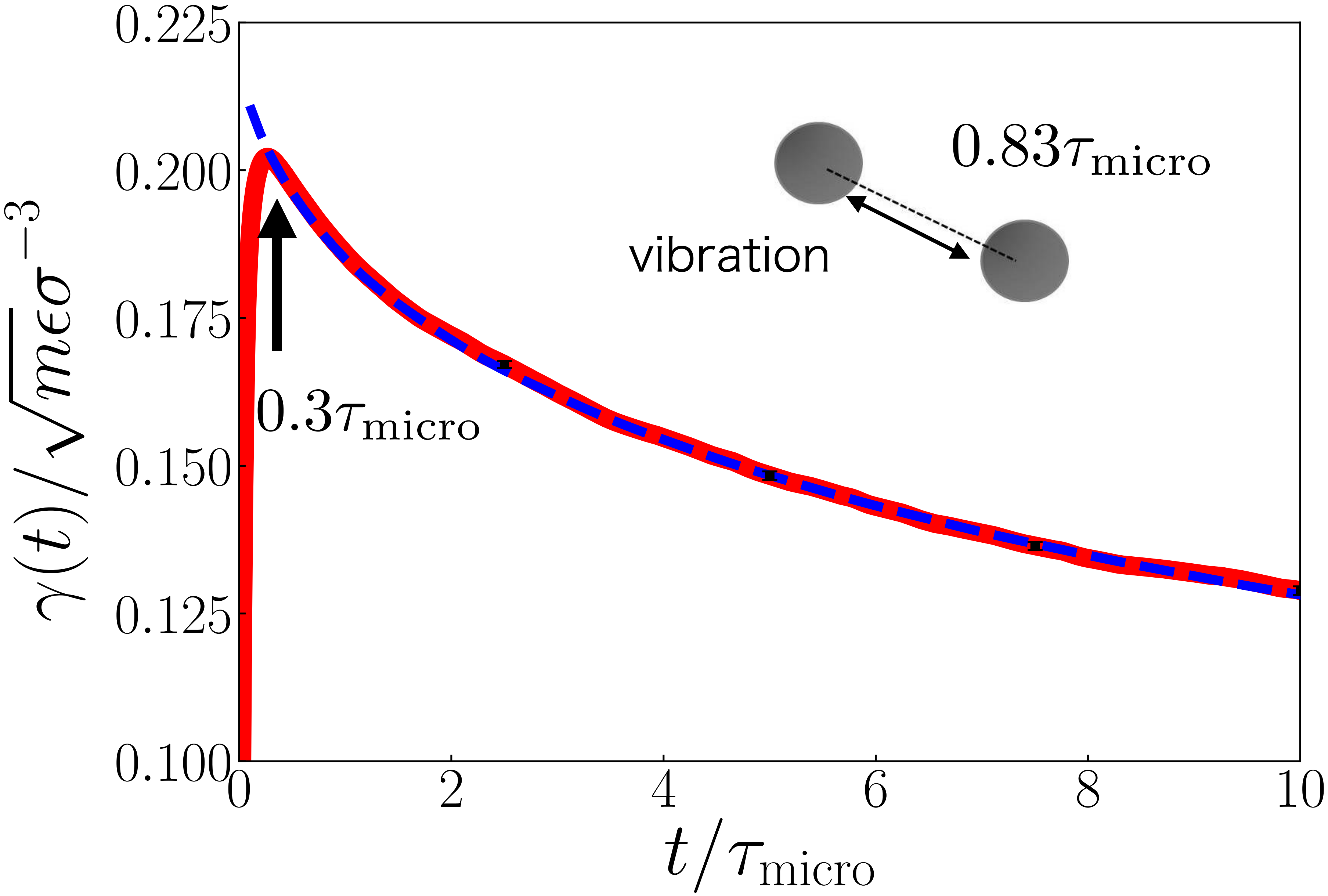


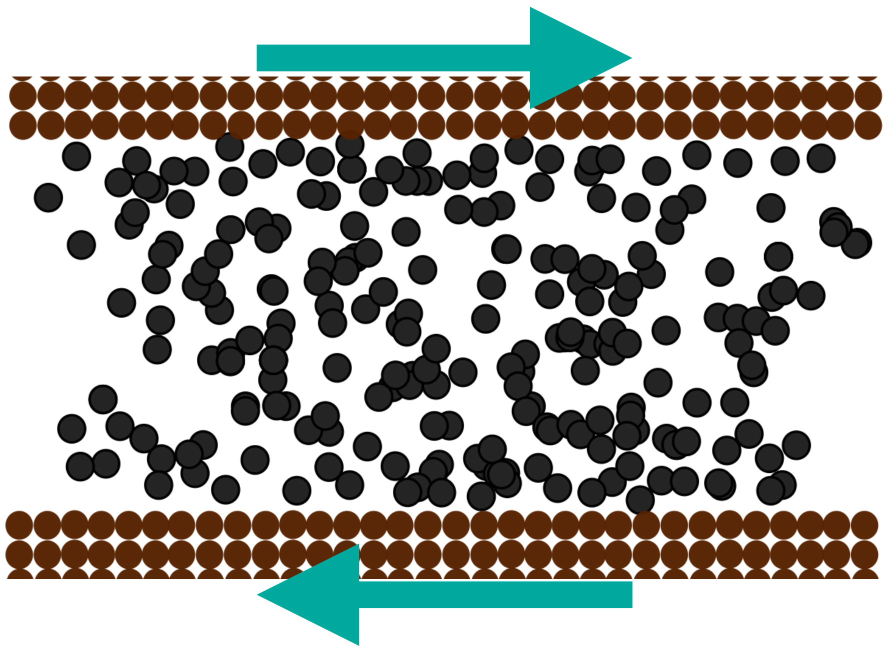
Fluctuating hydrodynamics accurately describes simulation data even in microscopic time scale.

Comparison with non-equilibrium measurement

Slip length is obtained in two different way.

1, best-fitting parameter of $\gamma(t)$

2, observation of velocity field in non-equilibrium steady state



c_{FS}	b_{neq}/σ	b_{eq}/σ
0.8	7.5	7.8
0.4	30.5	29.2
0.0	118 ± 7.5	104

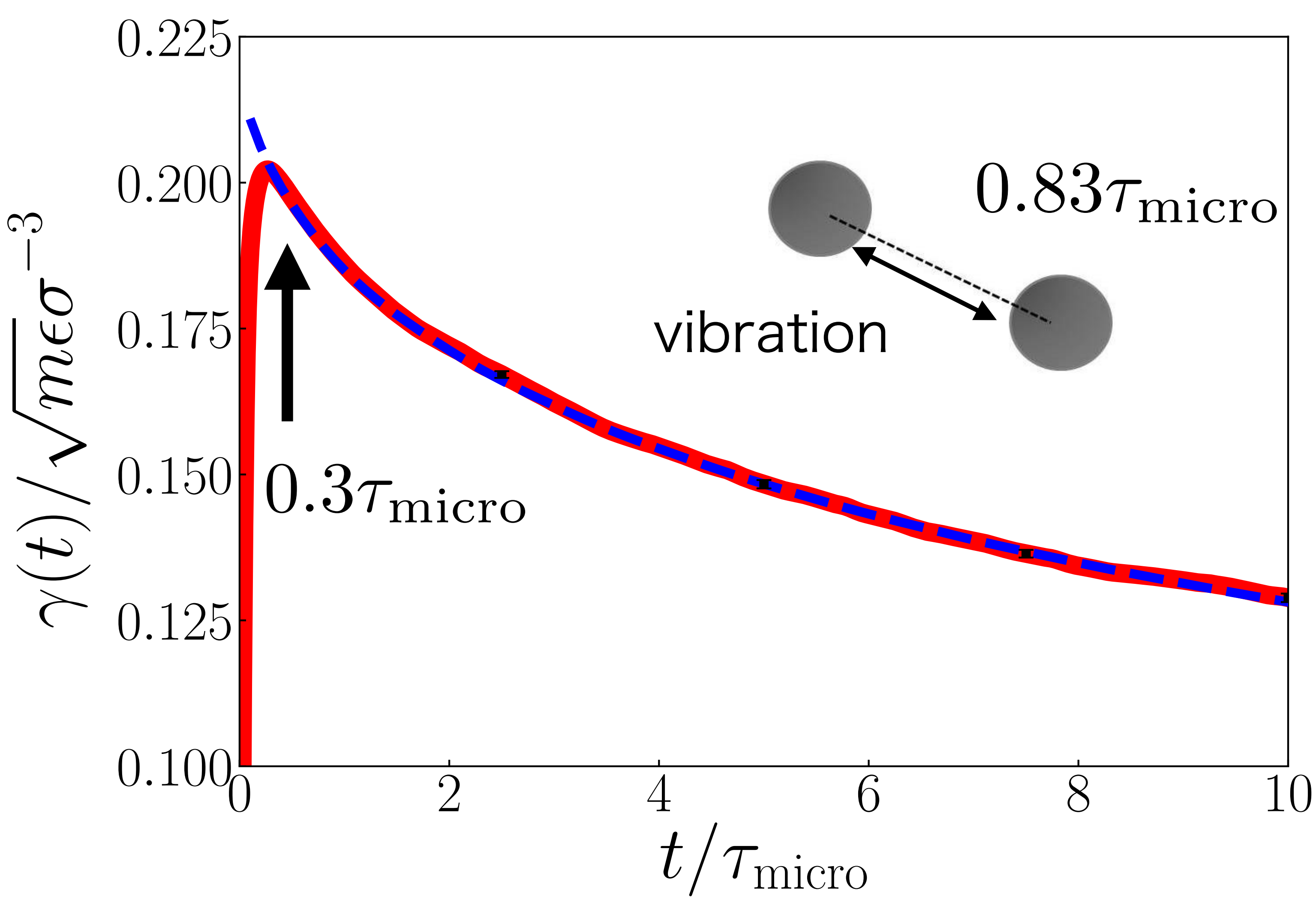
Deviations between NEMD and EMD simulations are within 10%.

Our goal：to establish relationship between slip length and molecular parameters(wall structure, fluid structure)

to extract information on slip length from $\gamma(t)$

We can obtain more information by analyzing linearized fluctuating hydrodynamics.

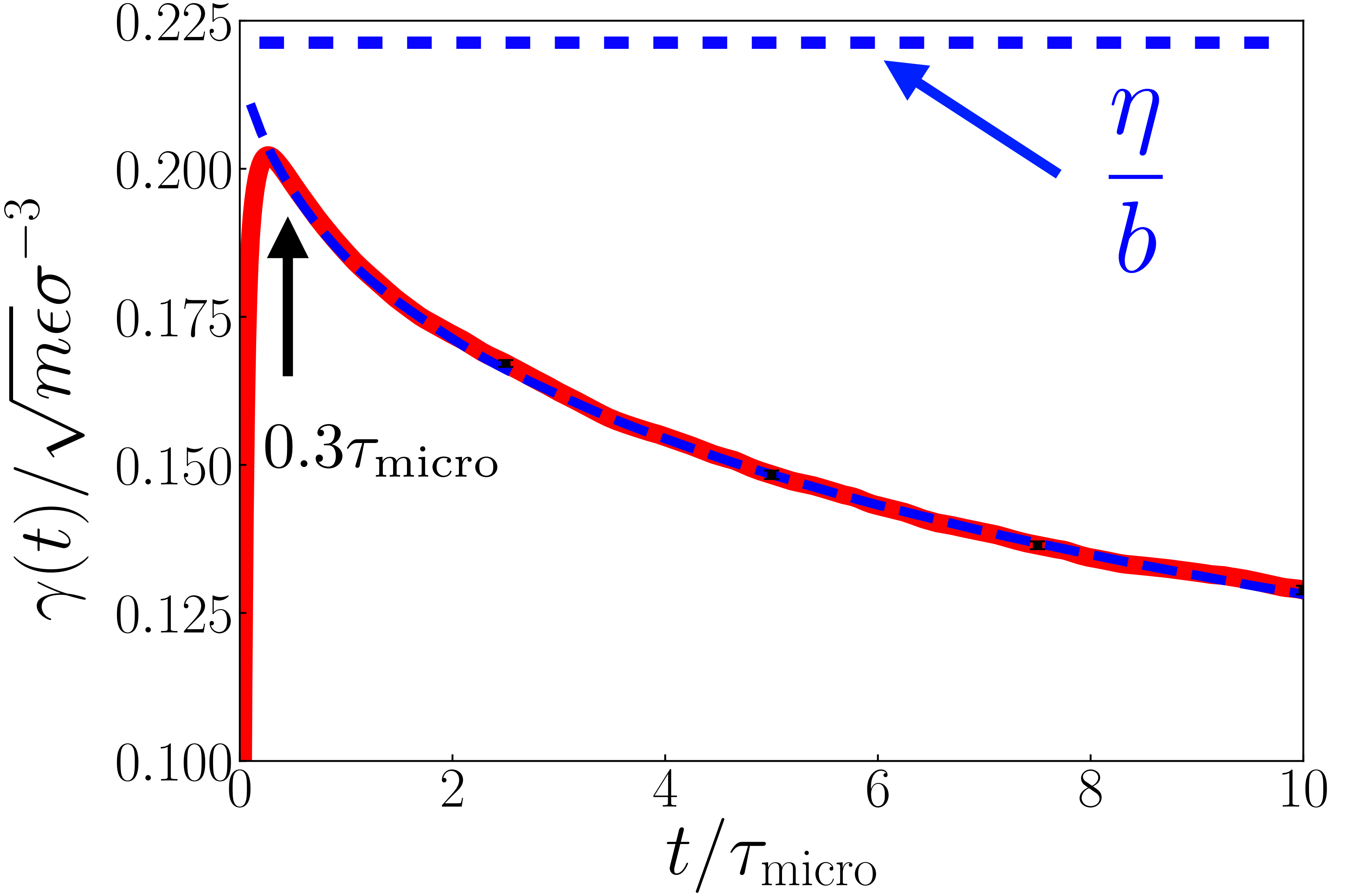
Application



Green-Kubo-like formula

Exact result of LFH

$$\lim_{t \to +0} \gamma(t) = \frac{\eta}{b}$$



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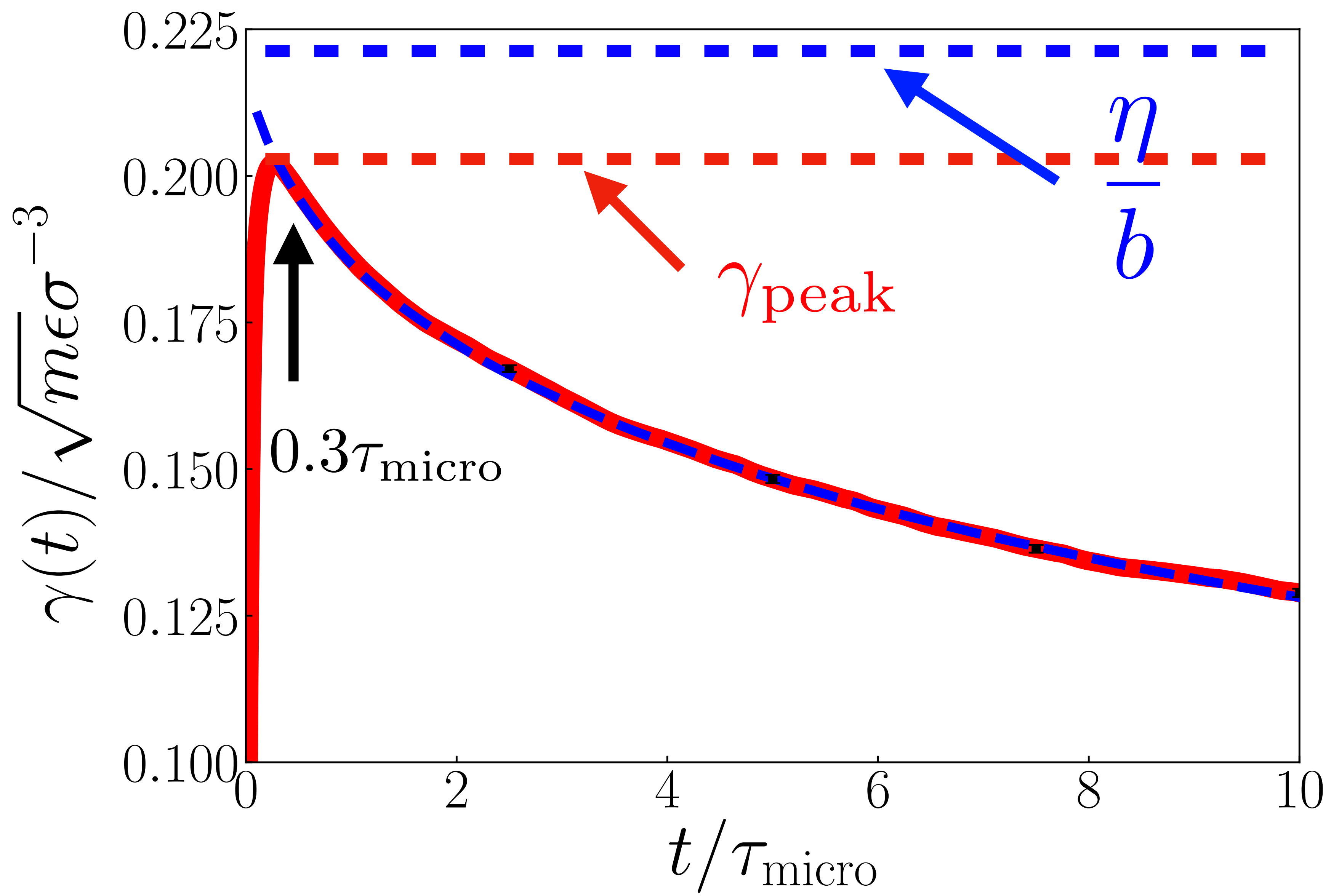
Reasonable estimation

$$\gamma_{\mathrm{peak}} \sim \frac{\eta}{b}$$

L. Bocquet and J.-L. Barrat, 1994



Application to rough wall

in progress

Our goal : to establish relationship between slip length and molecular parameters(wall structure, fluid structure)

Reasonable estimation

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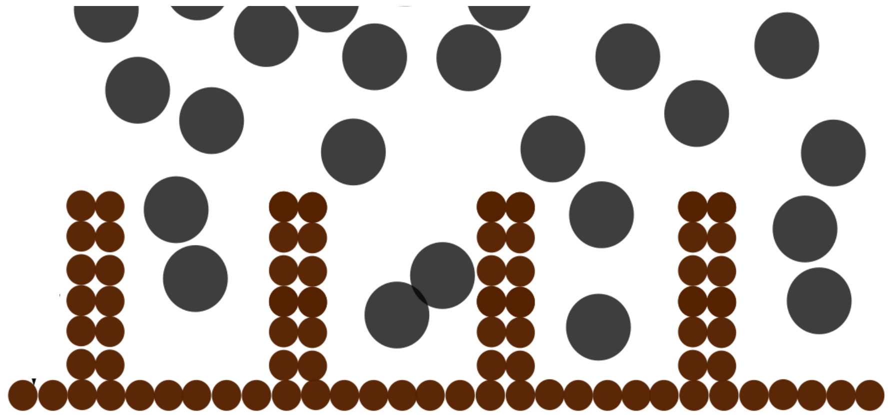

Rough wall

Our derivation expands the range of application.

When density of pillars are small, N_p/S (density of pillars)

$$\gamma_{\mathrm{peak}} = \frac{1}{k_B T S}\int_0^{\tau_0} ds \langle F_t(s) F_t(0)\rangle \simeq \gamma_{\mathrm{plate}} + \frac{N_p}{S}\gamma_{\mathrm{pillar}}$$

$$\Rightarrow \boxed{b \sim \frac{1}{\frac{1}{b_{\mathrm{plate}}} + \frac{N_p}{S}\frac{\gamma_{\mathrm{pillar}}}{\eta}}}$$

universal relation

Important conclusions

<u>GK formula</u>

$$\frac{\eta}{b} = \lim_{t\to\infty} \lim_{L\to\infty} \gamma(t)$$

macroscopic limit

infinite time limit

<u>Linearized fluctuating hydrodynamics</u>

provides description of $\gamma(t)$

in finite system

in full time region